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Photoconductivity of GaSe under high excitation

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Abstract : An investigation is presented of the photoconductivity in layered GaSe crystals in exciton resonance region at high optical excitations. Disappearance of the exciton peak in the photoconductivity and transmission spectra is due to the process of exciton-exciton interaction. The electron-hole pair density is about 3×10^{19} cm^{-3} which exceeds the exciton density necessary for the Mott transition in GaSe.

Keywords : Photoconductivity, GaSe crystals, exciton resonance region

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1. Introduction

Gallium selenide is a layered semiconductor of the III-VI family where each layer contains two gallium and two selenium close-packed sublayers in the stacking sequence Se-Ga-Ga-Se [1]. The bonding between two adjacent layers is of the Van der Waals type, while within the layer the bonding is predominantly covalent. Band structure calculations [1,2] predict the presence of an indirect minimum of the conduction band at the point M (M_3^+ symmetry) of the Brillouin zone lower than the direct minimum (Γ_4^-) at the point Γ. Moreover, the top of the valence band lies at the center of the Brillouin zone and has the symmetry Γ_3^+. The direct and indirect gaps are very close in energy. Measurements of optical absorption and of photoluminescence show a difference of about 25 meV between these two minima [3-7].

It is known that the long-wavelength absorption edge of GaSe corresponds with the state of exciton transitions [8-12]. Excitonic absorption can be easily seen at room temperature. Excitons in GaSe have a rather high binding energy E_{ex} = 20 meV. High concentrations of free carriers and excitons can be created in GaSe with intense laser beams. At these high concentrations, the interactions between the particles become important. Measurements of the luminescence and optical absorption in GaSe crystals show that, at high exciton densities exciton-exciton interactions take place [13-23].

To our knowledge, very few data are available in literature on the photoelectrical properties of GaSe. Previous photoconductivity measurements usually, were carried out either at rather low excitation [24] or with strongly absorbed (gap) radiation [25]. Therefore, experimental investigation of photoconductivity in GaSe crystals in the exciton resonance region at high optical excitations is of certain interest. The purpose of the photoconductivity measurements presented here is two-fold : first, they provide independent evidence for the disappearance of exciton absorption at high excitations induced by the exciton-exciton interaction; second, this is a simple method which eliminates difficulties encountered with optical measurements (for example, existence of spatial inhomogeneity of the excitation in the sample).

In this note, we present the preliminary experimental results of photoconductivity in GaSe crystals in the exciton resonance region at high optical excitations.

2. Experimental method

All photoconductivity measurements presented here were carried out on p-type GaSe grown by the Bridgman technique. The samples cleaved from the ingots had an area of 1 cm^2 and a thickness of 10-50 μm parallel to the C-axis. Ohmic contacts for photoelectrical measurements were obtained by depositing high-purity indium onto the samples. Mobility and concentration of charge carriers measured by conventional methods at room temperature were about 20 $cm^2/V.s$ and 1×10^{14} cm^{-3}, respectively.

As an excitation source, a Rhodamine 6G dye laser (PRA, LN-107) pumped by the output of a N_2-laser (PRA, LN 1000), tuned through the region (568-605) nm and (594-643) nm with a spectral width of 0.4 Å, a pulse power of 120 kW at a repetition frequency of 10 Hz and a pulse width of 1 ns was used. Laser beam density was varied by inserting calibrated neutral density filters. The incident light being perpendicular to the layer surfaces (|| C-axis) was focused into a spot of 0.1 mm. The applied field direction was perpendicular to the C-axis of the crystal. The output signals were detected by a recorder (HP-7475 A) through a storage oscilloscope (Le Croy 9400).

3. Results and discussion

The results for the excitation spectra of photoconductivity are given in Figure 1. At the lowest excitation, the well-known exciton peak is observed at 2.00 eV (curve 1). By increasing the laser intensity, the exciton peak is raised first (curve 2), then begins to diminish (curve 3) and disappears completely at higher intensities (curve 4). The transmission spectra of GaSe measured under the same experimental conditions is also indicative of a bleaching of exciton absorption at higher excitations. This is illustrated in the inset of Figure 1.

Dependence of the photoconductivity on the excitation power in the case of resonant excitation of excitons is shown in Figure 2. It is clear from the figure that photoconductivity is changed from a linear to a sublinear dependency within a rather extended region of intensities. By increasing the laser intensity further, photocurrent starts to decrease.

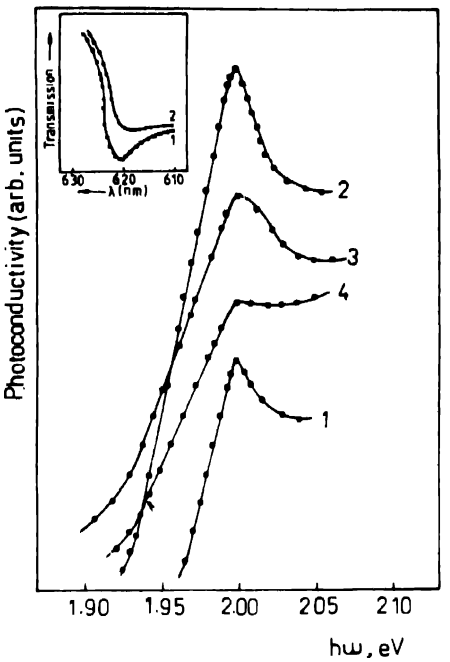

Figure 1. Photoconductivity spectra of GaSe (300 K) at various excitation powers (in MW/cm^2) : 1–0.3; 2–1; 3–5; 4–12; The inset shows transmission spectra for two levels of excitation (in MW/cm^2) · 1–0.1; 2–12.

The relaxation curves of photoconductivity as a function of the excitation show certain pecularities (Figure 3, a, b, c). At low excitation (~ 0.3 MW/cm^2), the decay time consists of fast and slow components (Figure 3a). The fast component is of the order of ~ 3×10^{-7} s which does not change upto 3 MW/cm^2, while the slow component is about a few microsecond. By increasing the intensity, the density of charge carriers contributing the slow component decreases with respect to that of the fast component (Figure 3b). When the excitation power exceeds ~ 3 MW/cm^2, the time duration of the fast component becomes small, ~ 10 ns (Figure 3c).

The above characteristics exhibited by GaSe samples may be explained by the process of exciton-exciton interaction leading to a complete breakdown of excitons [15-17, 21-23]. In fact, at low excitation levels, in the case of resonant excitation of excitons, small number of excitons having mutually weak interactions are created in GaSe. By increasing the laser intensity, the exciton density is raised leading in turn to a rise in photoconductivity. When the concentration of excitons reaches a critical value, strong interactions take place between excitons. This process limits the concentration of excitons and therefore, causing the photocurrent not to rise. The density of the absorbed photons at 4 MW/cm^2 averaged over the sample thickness in our experiment reached ~ 3×10^{19} cm^{-3} which exceeds the exciton

density necessary for the Mott transition in GaSe [16]. Analysis of the kinetics of the equations of photoconductivity for CdS show that at low excitations, photoconductivity changes linearly with the excitation intensity, but at high excitations when exciton-exciton

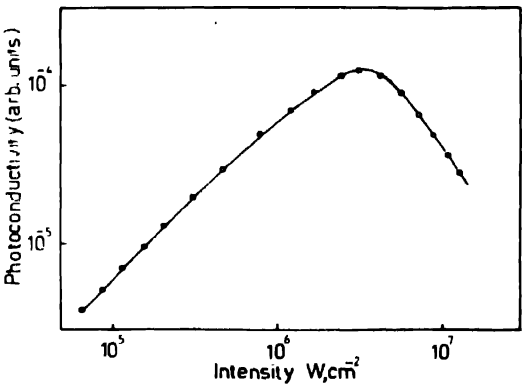

Figure 2. Dependence of the photoconductivity on the excitation power in the case of resonant excitation of excitons ($\hbar\omega$=2.00 eV).

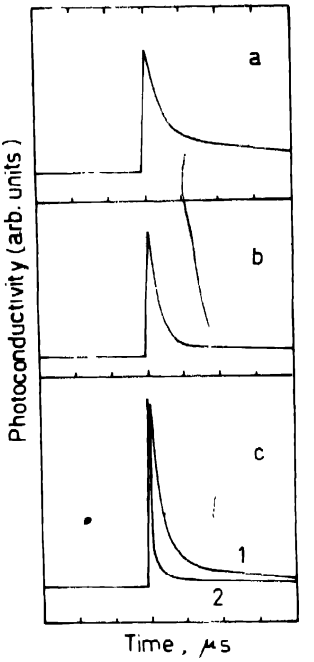

Figure 3. Relaxation curves of photo-conductivity at various excitation powers (in MW/cm^2) : a–0.3; b–3.9 (time per division 0.5 μs), c–6 (curve 1), 12 (curve 2) (time per division 0.2 μs).

interaction becomes dominant, the linear dependency is changed into a sublinear one [26,27]. Our experimental results concerning the photoconductivity in GaSe are in good agreement with the results of ref. [27] for excitations upto 3 MW/cm^2; but for higher excitations, photoconductivity starts to decrease (see Figure 2). The decrease in photoconductivity at higher excitation levels (> 4 MW/cm^2) may be due not only to the diminishing of the exciton absorption (due to exciton-exciton interaction process), but also to the diminishing of recombination life time of electron-hole pairs (due to the other processes such as two-photon absorption, absorption by the free charge carriers and [28] *etc*).

4. Conclusion

We have shown that the nonlinear exciton absorption in layered GaSe crystals caused by the exciton-exciton scattering process can be detected directly by photoconductivity measurements. Disappearence of the exciton peak in the photoconductivity spectrum occurs when the electron-hole pair density exceeds the exciton density necessary for Mott transition.

This method eliminates difficulties encountered with the standard optical techniques and can also be used to investigate exciton-exciton interaction process in other layered semiconductors (InSe, GaS,.....).

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